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A Review of Standards of Performance for New Stationary Sources - Nitric Acid Plants

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1.0 EXECUTIVE SUMMARY

The objective of this report is to review the New Source Performance Standard (NSPS) for nitric acid plants in terms of developments in control technology, economics and new issues that have evolved since the original standard was promulgated in 1971. The need for possible revisions to the standard is analyzed in the light of compliance test data available for plants built since the promulgation of the NSPS. The NSPS review includes the NO_x emission standard for the nitric acid plant production unit. While included in the nitric acid plant NSPS, the opacity standard is not reviewed separately since it is directly related to the NO_x standard. The following paragraphs summarize the results and conclusions of the analysis, as well as recommendations for future action.

1.1 Best Demonstrated Control Technology

A mixture of nitrogen oxides (NO_x) is present in the tail gas from the ammonia oxidation process for the production of nitric acid. In modern U.S. single pressure process plants producing 50 to 60 percent acid, uncontrolled NO_x emissions are generated at the rate of about 21 kg/Mg* of 100 percent acid (42 lb/ton) corresponding to approximately 3000 ppm NO_x (by volume) in the exit gas stream. The catalytic reduction process** has been largely supplanted by the extended absorption process as the control technology of choice for

*Mg - Metric tons.

**The process used in the rationale for the present NO_x NSPS as best demonstrated control technology.

controlling NO_x emissions from new nitric acid plants to the level required by the standard of performance.* The latter control system has apparently been chosen by the nitric acid industry due to the increasing cost and danger of shortages of the principal fuel (natural gas) used in the catalytic reduction process. Since the energy crisis of the mid-1970s, over 50 percent of the nitric acid plants that have come on stream through mid-1978, and almost 90 percent of the plants scheduled to come on stream through 1979, use the extended absorption process for NO_x control.

1.2 Current NO_x NSPS Levels Achievable with Best Demonstrated Control Technology

Fourteen of the new or modified operational nitric acid production units subject to NSPS showed compliance with the current NO_x control level of 1.50 kg/Mg (3 lb/ton).** The average of seven sets of test data from catalytic reduction-controlled plants is 0.22 kg/Mg (0.44 lb/ton), and the average of six sets of test data from extended absorption-controlled plants is 0.91 kg/Mg (1.82 lb/ton).*** All of the plants tested were in compliance with the opacity standard. It

*It should be noted that standards of performance for new sources established under Section 111 of the Clean Air Act reflect emission limits achievable with the best adequately demonstrated technological system of continuous emission reduction (taking into consideration the cost of achieving such emission reduction, as well as any nonair quality health and environmental impacts and energy requirements).

**Five units had not been tested for compliance as of mid-1978. No additional data have been obtained for this report since mid-1978.

***One set of data covers a nitric acid plant using a combination of chilled absorption and caustic scrubbing for NO_x control. This plant is in compliance.

appears that the extended absorption process, while it has become the preferred control technology for NO_x control, cannot control these emissions as efficiently as the catalytic reduction process. In fact, over half of the test results for extended absorption, while in compliance, were within 20 percent of the NO_x standard. A principal vendor of the extended absorption process only provides a 7 to 8 percent safety factor (in terms of absorber tray count) in the performance guarantee. Thus, the extended absorption process appears to have limitations with respect to NO_x control, and compares unfavorably with catalytic reduction in its ability to reduce NO_x emissions much below the present NSPS level. However, the overriding consideration which leads to the recommendation of no change in the NO_x NSPS at the present time, is the sharply escalating cost and developing long-term shortages of natural gas which have caused the present pronouced trend to the extended absorption process for NO_x control in new plants. It is also recommended that an in-depth, EPA study be carried out to completely define the NO_x control capability of this process before any future consideration can be given to making the current NO_x NSPS more stringent.

1.3 Economic Considerations Affecting the NO_x NSPS

Nitric acid plant operators opting for the extended absorption process for NO_x control for new plants (rather than catalytic reduction) would not be penalized from an economic standpoint, since the annualized costs of these two NO_x control methods appear to be

comparable. This is especially true now with the cost of fuel (natural gas) for the catalytic reduction process experiencing sharp rises. Capital cost, however, for this process is appreciably higher than that for catalytic reduction, thus, making the latter process less capital intensive. Making the NO_x standard more stringent at this time would severely impact the investment cost of the extended absorption process, since much larger absorption towers would have to be incorporated in new plants in order to meet performance guarantees.

1.4 Impact of Projected Growth of the Nitric Acid Industry on NO_x Emissions

Based on an estimated nitric acid plant growth rate of four new production lines per year between 1980 and 1983, a 50-percent reduction of the present NO_x NSPS level--from 1.5 kg/Mg (3 lb/ton) to 0.75 kg/Mg (1.5 lb/ton)--would result in a drop in the estimated percentage NO_x contribution of these new nitric acid plants to the total national NO_x emissions, from 0.02 to 0.01 percent.

1.5 Problems Encountered by the Extended Absorption Process in Meeting the NO_x NSPS

Based on limited data, problems are encountered with the extended absorption process in meeting the NO_x standard during certain startup periods and unscheduled shutdowns. During these periods, process conditions are unstable and NO_x concentrations tend to be high while nitric acid production is low or nonexistent so that 3-hour averaging is insufficient to bring the average NO_x level below 1.5 kg/Mg (3 lb/ton).

2.0 INTRODUCTION

In Section 111 of the Clean Air Act, "Standards of Performance for New Stationary Sources," a provision is set forth which requires that "The Administrator shall, at least every 4 years, review and, if appropriate, revise such standards following the procedure required by this subsection for promulgation of such standards." Pursuant to this requirement, the MITRE Corporation, under EPA Contract No. 68-02-2526, is to review 10 of the promulgated NSPS including the nitric acid plant production unit.

The main purpose of this report is to review the current nitric acid standards for NO_x and opacity and to assess the need for revision on the basis of developments that have occurred or are expected to occur in the near future. This report addresses the following issues:

1. A review of the definition of the present standards.
2. A discussion of the status of the nitric acid industry and the status of applicable control technology.
3. An analysis of NO_x and opacity test results and review of levels of performance of best demonstrated control technologies for emission control.
4. An analysis of the effect of projected nitric acid plant construction on NO_x emissions.
5. A study of problems encountered by recently developed NO_x control technology with the NSPS.

Based on the information contained in this report, conclusions are presented and specific recommendations are made with respect to changes in the NSPS.

3.0 CURRENT STANDARDS FOR NITRIC ACID PLANTS

3.1 Background Information

Prior to the promulgation of the NSPS in 1971, only 10 of the existing 194 weak nitric acid (50 to 60 percent acid) production facilities were specifically designed to accomplish NO_x abatement. Without control equipment, total NO_x emissions from nitric acid plants can range from 1000 to 6000 ppm by volume. In a typical plant, total NO_x emissions are approximately 3,000 ppm in the stack gas, equivalent to a release of 21.5 kg/Mg (43 lb/ton) of 100 percent acid produced (EPA, 1971).

At the time of the NO_x NSPS promulgation there were no state or local NO_x emission abatement regulations in effect in the U.S. which applied specifically to nitric acid production plants. Ventura County, California, had enacted a limitation of 250 ppm NO_x to govern nitric acid plants as well as steam generators and other sources (EPA, 1971).

In 1971, NO_x emission decolorization was practiced at 52 nitric acid plants by a method which also permitted maximum power recovery from the pressurized absorber tail gas. The uncontrolled NO_x tail gas emission consisted of approximately 50 percent nitrogen dixoide (NO_2), an opaque reddish-brown gas; and the remainder is colorless nitric oxide (NO). Through the use of a catalytic reduction technique, the aforementioned plants accomplished decolorization of the stack gas, i.e., the visible NO_2 is converted to

colorless NO in a highly exothermic reaction, with the heated exhaust gas from the catalytic treatment being then passed through an expander to recover power for driving the air-compressor turbine used in the nitric acid manufacturing process.

Stack gas decolorization enabled nitric acid plants in many areas to meet visible emission regulations (with equivalent opacity provisions), even though the catalytic decolorization technique has little effect on the total NO_x emissions (EPA, 1971).

It is estimated that NO_x emissions from nitric acid plants totalled 163,000 Mg (179,000 tons) in 1971 and 137,000 Mg (150,000 tons) in 1976 (Mann, 1978). This represented a 16 percent drop in NO_x emissions in the first 5 years after the promulgation of the NSPS and implementation of State Implementation Plans (SIPs) for this pollutant. By the end of 1977, nitric acid plants, in compliance with NSPS, represented an estimated 23 percent of the industry capacity.

3.2 Facilities Affected

The NSPS regulates nitric acid plants that were planned or under construction or modification as of August 17, 1971. Each nitric acid production unit (or "train") is the affected facility. The standards of performance apply to new facilities producing so-called "weak nitric acid" (defined as 50 to 70 percent strength). The standards do not apply to the various processes used to produce strong acid by extraction or evaporation of weak acid, or by the direct strong acid process.

An existing nitric acid plant is subject to the NSPS if: (1) it is modified by a physical or operational change in an existing facility thereby causing an increase in the emission rate to the atmosphere of any pollutant to which the standard applies, or (2) if in the course of reconstruction of the facility, the fixed capital cost of the new components exceeds 50 percent of the cost that would be required to construct a comparable entirely new facility that meets the NSPS.

3.3 Controlled Pollutants and Emission Levels

Total nitrogen oxide emissions from nitric acid plants are controlled under the NSPS, as defined by 40 CFR 60, Subpart G (as originally promulgated in 36 FR 24881 with subsequent modifications in 39 FR 20794):

> (a) On and after the date on which the performance test required to be conducted . . . is completed, no owner or operator subject to the provisions of this subpart shall cause to be discharged in to the atmosphere from any affected facility any gases which:
>
> (1) Contain nitrogen oxides, expressed as NO_2, in excess of 1.5 kg per metric ton of acid produced; (3.0 lb per ton), the production being expressed as 100 percent nitric acid.
>
> (2) Exhibit 10 percent opacity, or greater.

This standard was based on inspections and stack tests of existing nitric acid facilities; consultations with plant operators, designers, and state local control officials; and a review of the literature. Investigation of nitric acid plant control technology showed that catalytic reduction systems could successfully control tail gas nitrogen oxide emissions to levels within the proposed

standard of 1.5 kg NO_x/metric ton of 100 percent acid (3 lb/ton). A survey of 10 U.S. plants equipped with catalytic reduction systems showed that all plants either consistently achieved that NO_x level or could be operated or repaired to meet the proposed standard (EPA, 1971).

All of the facilities equipped with catalytic NO_x reduction devices were found to operate with no visible emissions. Thus, any facility meeting the mass NO_x limit will produce no visible emissions from the stack and therefore meet the promulgated opacity standard (EPA, 1971).

Section 4.0 dicusses alternative NO_x control technologies that have come into use by the nitric acid industry since the promulgation of the standard, or are under development. Chief among these new technologies, and one that has been widely used since the mid-1970s, is the extended absorption process.

3.4 Testing and Monitoring Requirements

3.4.1 Testing Requirements

Performance tests to verify compliance with the NO_x standard must be conducted within 60 days after the plant has reached its full capacity production rate, but not later than 180 days after the initial start-up of the facility (40 CFR 60.8). The EPA reference methods (40 CFR 60, Appendix A) to be used in conjunction with NO_x compliance testing include:

1. Method 7 for the concentration of NO_x
2. Method 1 for sample and velocity transverses

3. Method 2 for velocity and volumetric flow rate; and

4. Method 3 for gas analysis.

Each performance test consists of 3 runs, each consisting at least four grab samples taken at approximately 15-minute intervals. The arithmetic mean of the runs constitutes the value used to determine whether the plant is in compliance.

3.4.2 Monitoring Requirements

The NO_x levels in the tail gas from new nitric acid plants are required to be continuously monitored to provide: (1) a record of performance and (2) information to plant operating personnel such that suitable corrections can be made when the system is out of adjustment. Plant operators are required to maintain the monitoring equipment in calibration and to furnish records of excess NO_x emission values to the Administrator of EPA or to the responsible State agency as requested.

Measurement principles used in the continuous gas analysis instruments for NO_x are (Apple, 1978):

1. Photometric
2. Nondispersive infrared absorption
3. Ultraviolet absorption
4. Electrochemical
5. Chemiluminescent emission
6. On-stack (in-situ) absorption

A continuous NO_x analyser in wide use in the nitric acid industry is based on the principle of photometric analysis. This analyzer consists of a split-beam design in which the difference in light absorption by nitrogen dioxide (NO_2) is measured at two different wavelengths (a measuring wavelength and reference wavelength). A basic requirement for this measurement principle is that all the NO, which is transparent in the visible and ultraviolet regions, is quantitatively converted to NO_2 in the measuring instrument (Dupont, 1974).

The continuous monitoring system is calibrated using a known air NO_2 gas mixture as a calibration standard. Performance evaluation of the monitoring system is conducted using the EPA Method 7. In general, the system in use should satisfy the specifications as shown in 40 CFR 60, Appendix B, Performance Specification 2.

Excess NO_x emissons are required to be reported to EPA (or appropriate state regulatory agencies) for all 3-hour periods of excess emissions (or the arithmetic average of three consecutive 1-hour periods). Periods of excess emission are considered to occur when the integrated (or arithmetic average) plant stack NO_x emission exceeds the 1.5 kg/Mg (3 lb/ton) standard.

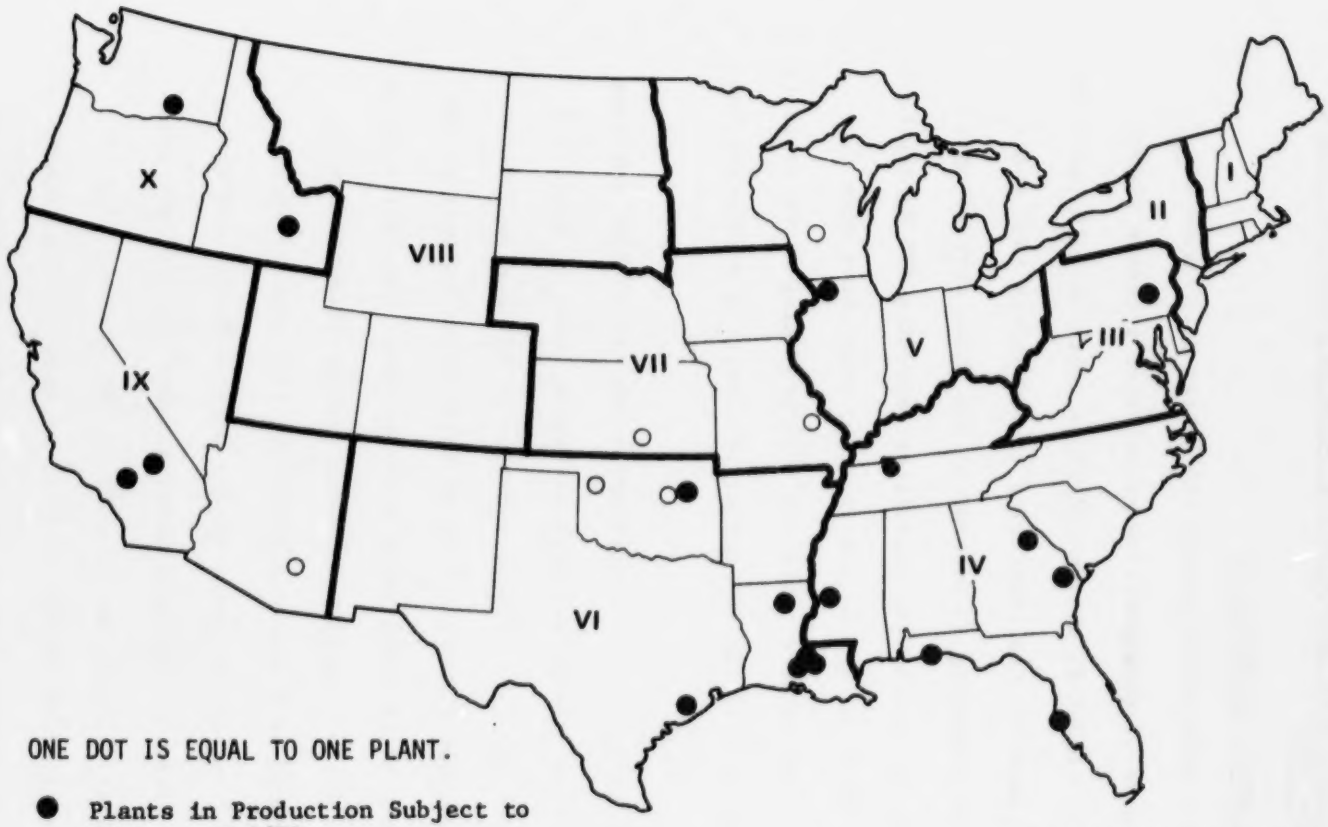
4.0 STATUS OF CONTROL TECHNOLOGY

4.1 Status of Nitric Acid Manufacturing Industry Since the Promulgation of the NSPS

4.1.1 Geographic Distribution

In 1972 there were approximately 125 nitric acid units in existence, exclusive of government-owned units at ordnance plants (Manderson, 1972). About 75 percent of these units were 10 years old or older and, in general, had capacities of 270 Mg/day (300 tons/day) or less. The remaining 25 percent of the units were of more recent and larger design, having capacities exceeding 270 Mg/day (300 tons/day). The Bureau of the Census reported that there were 72 plants (involving one or more units) in 1972 producing nitric acid in the U.S. and that by 1977 the net number of plants in production had increased by only one.

As of June, 1978, 19 nitric acid units subject to NSPS had come on stream. Table 4-1 summarizes data presented later in Table 4-4 for these 19 units and their design tonnage by EPA region. Figure 4-1 shows the geographic distribution of these units as well as the locations of eight units still under construction. The latter units are described in Table 4-2. The heaviest concentration of new or modified nitric acid unit construction since 1971 appears in EPA Regions IV and VI--along the coast of the Gulf of Mexico and within the Mississippi River delta. Additionally, about half of the total number of nitric acid plants are located in the southern tier of states. The distribution of nitric acid, as shown in Figure 4-1 displays a spacial pattern similar to that of the major fertilizer



SOURCE: MITRE CORP., 1978.

FIGURE 4-1
NITRIC ACID PLANTS BUILT OR UNDER CONSTRUCTION AFTER 1971

TABLE 4-1

NITRIC ACID PLANT COMPLETIONS SUBJECT TO NSPS

EPA Region	New or Modified Units in Production (1971-1977)	New or Modified Plant Design Capacity (100% HNO_3) Mg/day (tons/day	Percent of Total New or Modified Design Capacity
III	1	164(180)	2.0
IV	7	3936(4325)	47.8
VI	7	3265(3588)	39.6
IX	2	319(350)	3.9
X	2	549(603)	6.7
Total	19	8319(9046)	100.0
Average Design Capacity/Unit:		438(476)	

production centers (Chapman, 1973). Since the bulk of all nitric acid produced is consumed captively in the manufacture of nitrogen fertilizer used mainly in the Midwest cornbelt, the South Central states, and the Southwest, the similarity in spacial patterns between nitric acid plants and fertilizer manufacturing plants is to be expected.

4.1.2 Production

EPA predicted the start-up of five new nitric acid units per year for several years after promulgation of the NSPS (EPA, 1971). The actual average rate of start-up between 1971 and 1977 has been between two and three units per year.

In 1971, U.S. production of 100 percent nitric acid totalled 6,951,000 metric tons and increased at an average annual rate of 0.7

TABLE 4-2

NITRIC ACID PLANTS PLANNED OR UNDER CONSTRUCTION

Region	Company	Plant Location	Plant Capacity Mg/day (tons/day)	NO_x Control Technology	Anticipated Start-Up Date	Source
V	N-Ren Corp.	East Dubuque, Ill.	200 (220)	Extended Absorption	Dec., 1978	Coop, 1978
V	Badger Army Arsenal	Baraboo, Wis.	364 (400)	Extended Absorption	Dec., 1979	Dezariac, 1978
VI	Agrico Chemical Co.	Catoosa, Okla.	570 (630)	Chilled Absorption & Caustic Scrubbing	May, 1979	Murphy, 1978
VI	Terra Chemicals	Woodward, Okla.	248 (272)	Extended Absorption	Nov., 1978	Read, 1978
VII	U.S.S. Agricultural Chemicals	Crystal City, Mo.	500 (550)	Extended Absorption	Dec., 1978	Giles, 1978
VII	Sunflower Army Arsenal	DeSoto, Kans.	273 (300)	Extended Absorption	Nov., 1978	Dezariac, 1978
VII	Gulf Chemical Co.	Jayhawk, Kans.	546 (600)	Extended Absorption	Feb., 1980	Russell, 1978
IX	Apache Powder Co.	Benson, Ariz.	270 (300)	Extended Absorption	Dec., 1978	Baker, 1978

percent to 7,167,000 metric tons in 1977. Figure 4-2 shows the growth of nitric acid production from 1939, and Table 4-3 shows the percent change per year.

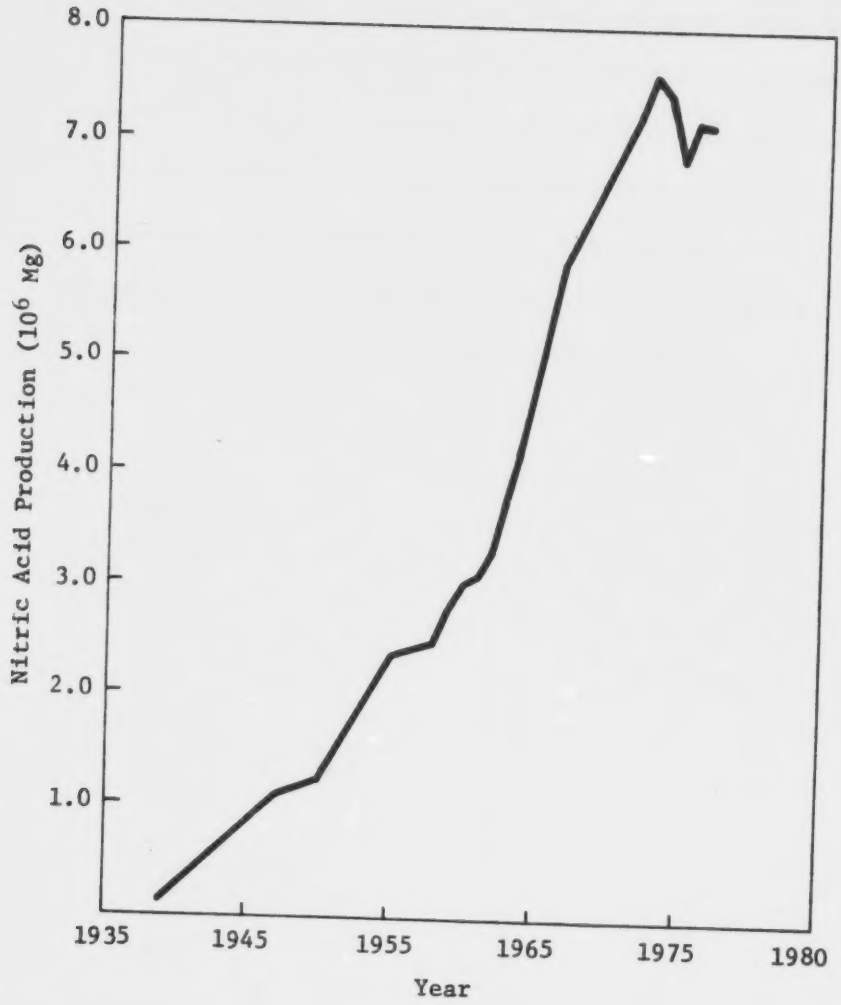
Major end uses for nitric acid are shown in Figure 4-3. The largest consumer of nitric acid is the fertilizer industry which consumes 70 percent of all nitric acid produced; industrial explosives use 15 percent of acid produced (Manderson, 1972). Other end uses of nitric acid are gold and silver separation, military munitions, steel and brass pickling, photoengraving, production of nitrates, and the acidulation of phosphate rock.

TABLE 4-3

U.S. NITRIC ACID PRODUCTION

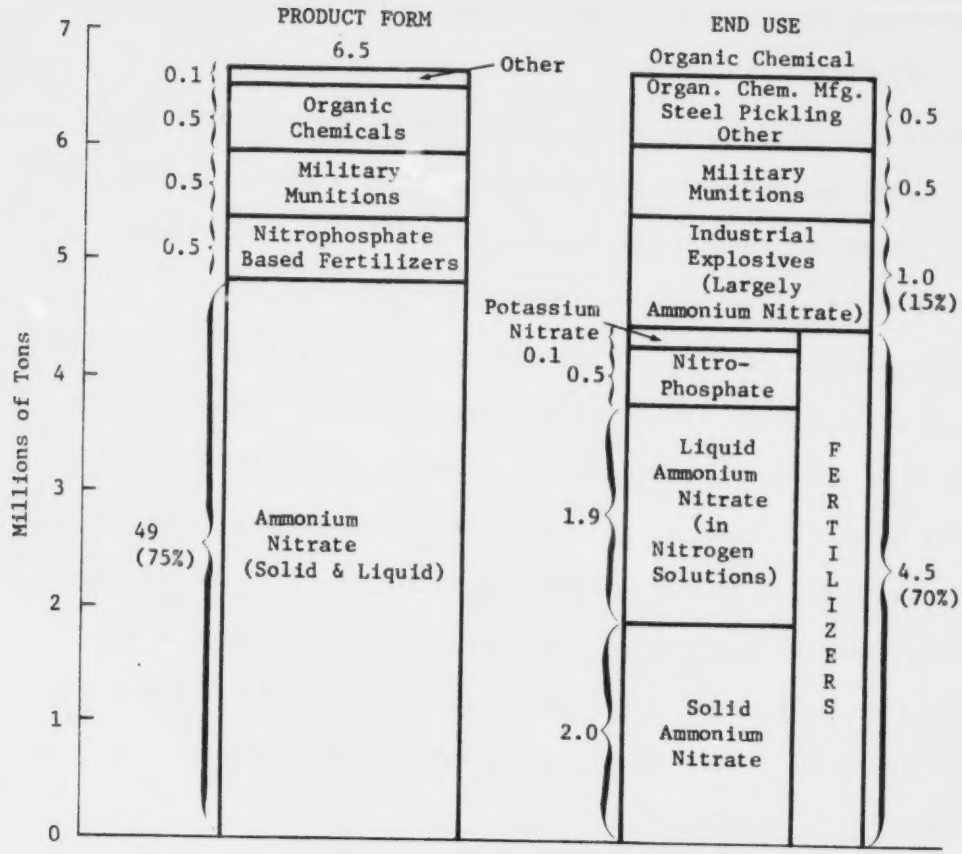
Year	Production of 100% Acid (10^6 Mg)	Annual Change (%)
1957	2.4	
1958	2.5	4.1
1959	2.8	12.0
1960	3.0	7.1
1961	3.1	3.3
1962	3.3	6.4
1963	3.6	9.0
1964	4.3	19.4
1965	4.7	9.3
1966	5.0	6.3
1967	5.8	16.0
1968	6.2	6.8
1969	6.6	6.4
1970	6.8	3.0
1971	6.9	1.4
1972	7.2	4.3
1973	7.6	5.5
1974	7.3	-3.9
1975	6.8	-6.8
1976	7.1	4.4
1977	7.1	0

Sources: Bureau of the Census, 1965; 1977.



Sources: Bureau of the Census, 1965; 1977.

FIGURE 4-2
GROWTH OF THE NITRIC ACID INDUSTRY



Source: Manderson, 1972.

FIGURE 4-3
NITRIC ACID CONSUMPTION IN THE U.S. BY MAJOR USES, 1970 (IN MILLIONS OF TONS OF 100% NITRIC ACID)

4.1.3 Trends

The average rate of production increase for nitric acid fell from 9 percent/year in the 1960-1970 period to 0.7 percent from 1971 to 1977. The decline in demand for nitric acid parallels that for nitrogen-based fertilizers during the same period (Bureau of the Census, 1977).

Nitric acid production shows an increasing trend towards plant/unit location and growth in the southern tier of states. In 1971, 48 percent of the national production was in the south. This figure increased to 54 percent in 1976 (Bureau of the Census, 1977).

About 50 percent of plant capacity in 1972 consisted of small to moderately sized units (50 to 300-ton/day capacity). Because of the economics of scale some producers are electing to replace their existing units with new, larger units (Manderson, 1972). Also, the trend toward reduction of NO_x emissions is stimulating the shutdown and replacement of older units. New nitric acid production units have been built as large as 910 Mg/day (1000 tons/day). The average size of new units is approximately 430 Mg/day (500 tons/day).

4.2 Nitric Acid Manufacture*

Nitric acid is manufactured in the U.S. by the high temperature catalytic oxidation of ammonia. The essential components of an ammonia oxidation nitric acid plant are:

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*Process information in Sections 4.2, 4.3 and 4.4 is taken from Acurex/Aerotherm, 1977, unless otherwise noted.

1. Converter or oxidation section where the ammonia vapor and air are mixed and reacted catalytically to oxidize the ammonia.

2. Cooler-Condenser section where the nitrogen dioxide is produced by cooling the reaction gases and weak nitric acid is formed.

3. Absorber section where the cool nitrogen dioxide is absorbed in water to form nitric acid.

In the first step of this process one volume of anhydrous ammonia is mixed with nine volumes of preheated air and passed through a multi-layered, silk fine platinum-rhodium gauze catalyst at 750° to 800°C. Under these conditions, the oxidation of ammonia to nitric oxide proceeds in an exothermic reaction with a 95 percent yield:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (1)$$

The second step involves the oxidation of the nitric oxide to nitrogen dioxide:

$$2NO + O_2 \rightarrow 2NO_2 \rightarrow N_2O_4 \qquad (2)$$

The forward rate of reaction (2), which is rather slow compared with reaction (1), is favored at lower temperatures and higher pressures. Hence, reaction (2) is always carried out after cooling the gas to 38°C or less and, depending on the process design, at pressures up to 500 kPa* (73 psig).

In the final step, the nitrogen dioxide/dimer mixture is cooled further and passed to an absorber where it reacts with water to produce an aqueous solution of 50 to 60 percent nitric acid, the concentration depending on the temperature, pressure, number of absorption

*Kilopascal - 100 kPa = approximately 1 atm.

stages, and concentration of the nitrogen dioxide entering the absorber

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \qquad (3)$$

This reaction is also favored by low temperature and high pressure, because the gases involved are more soluble at lower temperatures and absorption results in a reduction in volume. In fact, some processes utilize the low temperature/high pressure conditions to increase yields.

The formation of nitric acid in Equation (3) involves the disproportionation of nitrogen dioxide to form two moles of nitric acid for every mole of nitric oxide. In order to reoxidize the nitric oxide during absorption, secondary air (also known as bleacher air) is introduced into the absorber along with the nitrogen dioxide. However, the reaction to form nitric acid is never quite complete -- the overall process is 95 percent efficient, so that a small quantity of nitrogen oxides, NO_x (NO_2 and NO), is inevitably present in the waste gas discharged from the absorption column. The NO_x in these waste gases is the target for air pollution regulations and control.

Acid product is withdrawn from the bottom of the tower in concentrations of 55 to 65 percent. The air entering the bottom of the tower serves to strip NO_2 from the product and to supply oxygen for reoxidizing the NO formed in making nitric acid (Equation 3).

The oxidation and absorption operations can be carried out at low pressures (100 kPa), medium pressures (400 to 800 kPa) or high pressures (1000 to 1200 kPa). Both operations may be at the same pressure or different pressures.

Before corrosion-resistant materials were developed (precluding the use of high pressures) the ammonia oxidation and absorption operations were carried out at essentially atmospheric pressure. The advantages over higher pressure processes were longer catalyst life (about 6 months) and increased efficiency of ammonia combustion. However, because of the low absorption and NO oxidation rates, much more absorption volume was required, and several large towers were placed in series. Some of these low pressure units are still in operation, but they represent less than 5 percent of the current U.S. nitric acid capacity.

Combination pressure plants carry out the ammonia oxidation process at low or medium pressure and the absorption step at medium or high pressure. The increased pressure for the oxidation reaction shortens the catalyst's lifetime (1 to 2 months) and lowers the ammonia oxidation conversion efficiency. Thus, lower pressures in the oxidation process are preferred. On the other hand, higher pressures in the absorption tower increase the absorption efficiency and reduce NO_x levels in the tail gas. The advantages of higher absorber pressures must be weighed against the cost of pressure vessels and compressors.

The choice of which combination of pressures to use is very site specific and is governed by the economic tradeoffs such as costs of raw materials, energy and equipment and process efficiency. In the 1960s combination low pressure oxidation/medium pressure absorption and single pressure (400 to 800 kPa) plants were preferred. Since the 1970s the trend has been toward medium pressure oxidation/high pressure absorption plants in Europe and single pressure (400 to 800 kPa) plants in the U.S.

The two types of weak nitric acid production processes in use in new U.S. plants, i.e., single pressure and dual pressure process, are described in the following sections. Table 4-4 lists all of the new and modified nitric acid plants subject to NSPS, together with their capacities and the production and NO_x abatement processes used.

4.2.1 Single Pressure Process

In the single pressure process both the oxidation and absorption are carried out at the same pressure--either low (atmospheric) or medium pressures of 400 to 800 kPa (60 to 120 psig). Single pressure plants are the most common type in the U.S. Figure 4-4 is a simplified flow diagram of a single pressure process. A medium pressure process will be described in the following paragraphs.

Air is compressed, filtered, and preheated to about 300°C (592°F) by passing through a heat exchanger. The air is then mixed with anhydrous ammonia, previously vaporized in a continuous-steam

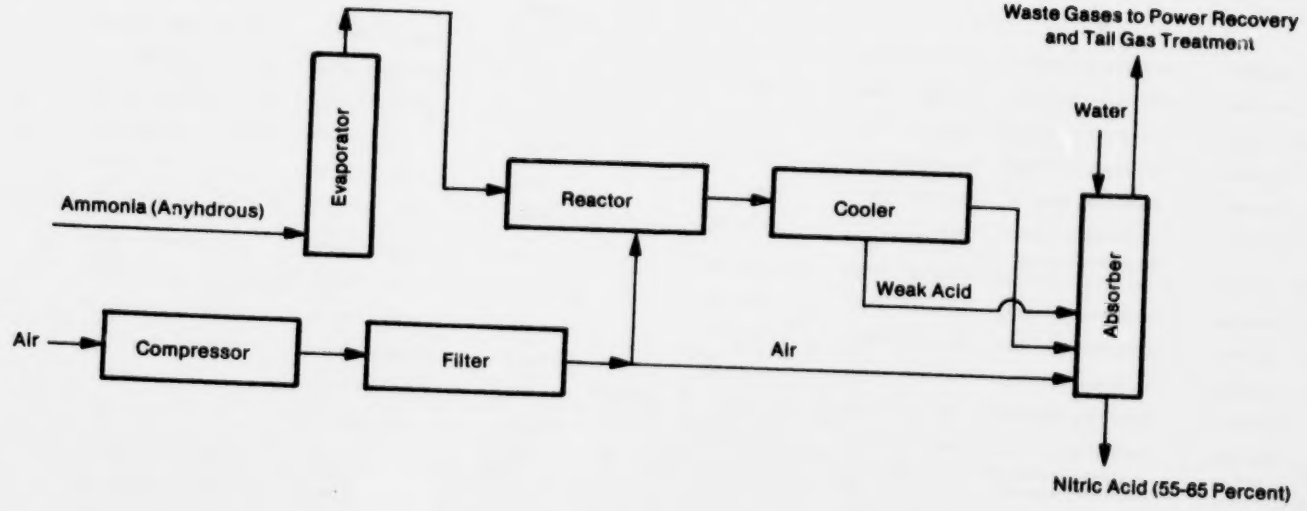
TABLE 4-4

NITRIC ACID PLANTS COMPLETED SINCE PROMULGATION OF THE NSPS

EPA Region	Company	Plant Location	Year Completed	No. of Units	Plant Design Capacity (100% HNO_3) Mg/day (tons/day)	Process Design	Emission Control System	Reference
III	Allied Chemical Corp.	Newell, Pa.	1975	1	164 (180)	Single Pressure	Catalytic Reduction	Bland, 1978
IV	Monsanto Textile Co.	Escambia City, Fla.	1977	1	819 (900)	Dual Pressure	[a]	Vick, 1978
	Nitram, Inc.	Tampa, Fla.	1976	1	310 (350)	Single Pressure	Catalytic Reduction	Thompson, 1978
	Kaiser Aluminum & Chem.	Savannah, Ga.	1976	1	450 (500)	Single Pressure	Extended Absorption	EPA CDS, 1978[b]
	Columbian Nitrogen	Augusta, Ga.	1977	1	819 (900)	Single Pressure	Catalytic Reduction	Gardner, 1978
	Mississippi Chemical	Yazoo City, Miss.	1977	1	910 (1000)	Dual Pressure	Extended Absorption	Stark, 1978
	U.S. Army	Holston, Tenn.	1973	1	328 (360)	Single Pressure	Extended Absorption	Brown, 1978
VI	CF Industries	Donaldsonville, La.	1976	1	285 (315)	Dual Pressure	Extended Absorption	Dezariac, 1978
	IMC - Dixie Chemical	Sterlington, La.	1977	1	470 (520)	Dual Pressure	Extended Absorption	Carville, 1978
	Rubicon Chemical Inc.	Geismar, La.	1976	1	200 (220)	Single Pressure	Extended Absorption	EPA CDS, 1978
	Allied Chemical Corp.	Geismar, La.	1976	1	320 (350)	Single Pressure	Catalytic Reduction	EPA CDS, 1978
	Agrico Chemical Co.	Catoosa, Okla.	1978	1	500 (550)	Single Pressure	Extended Absorption	Dessert, 1978
	Air Products & Chemical	Pasadena, Tex.	1975	1	570 (630)	Single Pressure	Chilled Absorption & Caustic Scrubbing	Murphy, 1978
	Dupont Co.	Victoria, Tex.	1976	1	289 (318)	Single Pressure	Catalytic Reduction	Spruiell, 1978
IX	Union Oil Co. of Calif.	Brea, Calif.	1977	1	918 (1000)	Single Pressure	Extended Absorption	Russell, 1978
	Valley Nitrogen	Fresno, Calif.	1977	1	137 (150)	Single Pressure	Catalytic Reduction	Waddell, 1978
X	J.R. Simplot Co.	Pocatello, Idaho	1977	1	180 (200)	Single Pressure	Catalytic Reduction	Kelly, 1978
	Chevron Chemical Co.	Kennewick, Wash.	1977	1	50 (53)	Single Pressure	Catalytic Reduction	Wolleson, 1978
			1977	1	500 (550)	Single Pressure	Extended Absorption	Spaniel, 1978
			TOTALS	19	8319 (9046)			
			AVERAGE		438 (476)			

[a] Controls not yet determined.

[b] Compliance Data System.



Source: Aerotherm, 1977

Reactor and Absorber Operate at the Same Pressure:

Low Pressure (≈Atmospheric) or Medium Pressure (≈60-120 psi)

FIGURE 4-4
SINGLE PRESSURE NITRIC ACID MANUFACTURING PROCESS

evaporator. The resulting mixture, which contains about 10 percent ammonia by volume, is passed through the reactor. The reactor contains a platinum-rhodium (2 to 10 percent rhodium) wire-gauze catalyst (e.g., 80 mesh and 75-mm diameter wire, packed in layers of 10 to 30 sheets) so that the gas travels downward through the gauze sheets. Catalyst operating temperature is about 750°C (1382°F). Contact time with the catalyst is about 3×10^{-4} second.

The hot nitrogen oxides and excess air mixture (about 10 percent nitrogen oxides) from the reactor are partially cooled in a heat exchanger and further cooled in a water cooler. The cooled gas is introduced into a stainless-steel absorption tower with additional air for the further oxidation of nitrous oxide to nitrogen dioxide. Small quantities of water are added to hydrate the nitrogen dioxide and also to scrub the gases. The overhead gas from the tower is reheated by feed/effluent heat exchangers and then expanded through a power recovery turbine/compressor used to supply the reaction air.* The bottom of the tower yields nitric acid of 55 to 65 percent strength. Fifteen of the 19 U.S. nitric acid plants subject to NSPS, employ a single pressure process.

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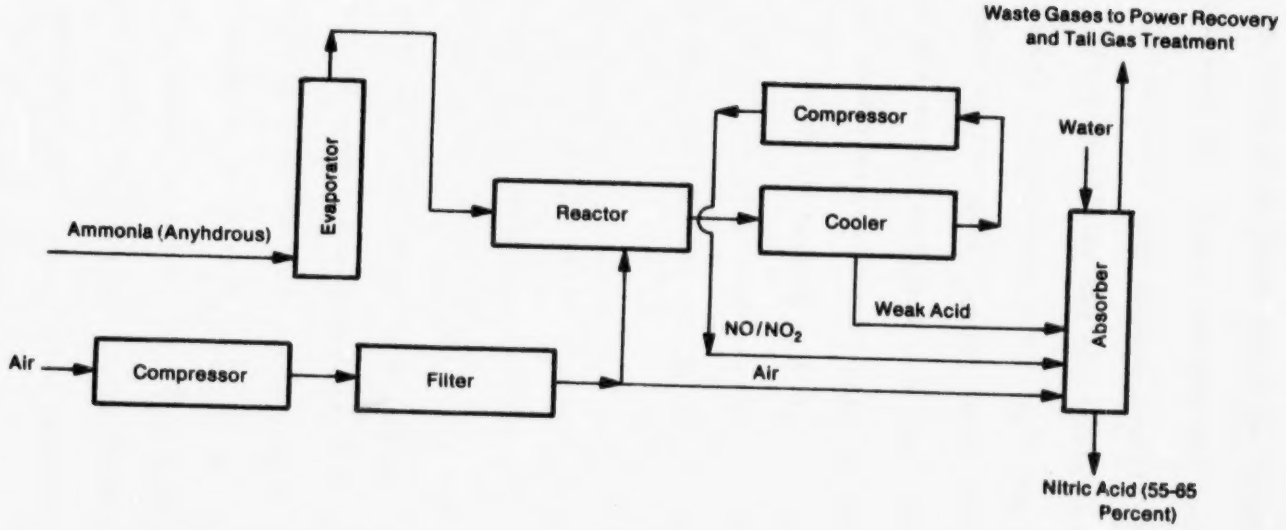
*In those plants using catalytic reduction as NO_x abatement method, the tail gas is first passed through the catalytic reduction system and then expand ed through a power recovery turbine/compressor used to supply the reaction air.

4.2.2 Dual Pressure Process

In order to obtain the benefits of increased absorption (with greater product yield) and reduced NO_x emissions, some dual pressure plants are in use in the U.S. Four of these plants subject to NSPS have been built in the U.S. Recent trends favor moderate pressure oxidation and high pressure absorption.

A simplified process flow diagram for a dual pressure plant is shown in Figure 4-5. In the Uhde version of this process, liquid ammonia is vaporized by steam, heated and filtered before being mixed with air from the air/nitrous oxide compressor at from 300 to 500 kPa (~3 to 5 atm.). The ammonia/air mixture is catalytically oxidized in the reactor with heat recovery by an integral waste heat boiler to generate steam for use in the turbine-driven compressor. The combustion gases are further cooled by tail gas heat exchange and water cooling before compression to the absorber pressure of 800 to 1400 kPa (~8 to 14 atm). The absorption tower is internally water cooled to increase absorption by water. Nitric acid up to 70 percent concentration is withdrawn from the bottom of the column and degassed with the air feed to remove unconverted NO before being sent to storage. The air/NO mixture is combined with reactor effluent to form the absorber feed. High yields of up to 96 percent conversion can be obtained by this process.



Source: Acurex/Aerotherm, 1977.

Reactor Pressure: 50-75 Psi
Absorber Pressure: 120-210 Psi

FIGURE 4-5
DUAL PRESSURE NITRIC ACID MANUFACTURING PROCESS

4.3 Emissions from Nitric Acid Plants

The main source of atmospheric emissions from the manufacture of nitric acid is the tail gas from the absorber tower. The emissions are primarily nitric oxide and nitrogen dioxide with trace amounts of nitric acid mist. Each of these pollutants has an effect on the color and opacity of the tail gas plume. The presence of nitrogen dioxide is indicated by a reddish-brown color. Since nitric oxide is colorless, the intensity of the color and, therefore, plume opacity, is directly proportional to the nitrogen dioxide concentration in the plume. Concentrations of greater than 0.13 percent by volume of nitrogen dioxide produce a definite reddish-brown color in the exit plume, whereas effluent gases containing less than 0.03 percent nitrogen dioxide are colorless.

The opacity of the plume is also a function of the amount of nitric acid mist in the tail gas, which is dependant on the type of process used, the extent of mist entrainment and the efficiency of entrainment separators. For those acid processes operated above atmospheric pressure, the tail gases are reheated and expanded for power recovery purposes and discharged to the atmosphere at 200° to 250°C. At this temperature, any acid mist present is converted to the vapor state. In atmospheric pressure processes, however, the temperature of the tail gas is below the dew point of nitric acid. As a result, the acid is emitted as a fine mist which increases the plume opacity.

The average emission factor for uncontrolled acid plants is 20 to 28 kg NO_x/Mg of acid, with typical uncontrolled tail gas concentrations on the order of 3000 ppm NO_x. This concentration would be experienced in a low pressure plant. The NO_x concentration in the tail gas of medium pressure plants ranges from 1000 to 2000 ppm.

Nitrogen oxide emissions vary considerably with changes in plant operation. Several operating variables have a more significant effect on increasing NO_x emissions. These include: (1) insufficient air supply to the oxidizer and absorber; (2) low pressure, especially in the absorber; (3) high temperatures in the cooler-condenser and absorber; (4) production of an excessively high-strength product acid; and (5) operation at high throughput rates. Finally, faulty equipment, such as compressors or pumps, lead to lower pressures and leaks which decrease plant efficiency and increase emissions.

4.4 Control Technology for NO_x Emissions from Nitric Acid Plants

Nitric acid plants can be designed for low NO_x emission levels without any add-on control equipment. Such plants are usually equipped with high efficiency absorbers, i.e., those having high inlet gas pressures and effective cooling of the absorber solution. However, all new U.S. plants built since the promulgation of the NSPS are designed to meet the low NO_x emissions required by the present standards with some form of NO_x abatement equipment.

A number of methods are available for reducing NO_x emissions from new nitric acid plants. These methods include catalytic

reduction with certain fuels, extended absorption, wet scrubbing, chilled adsorption, and molecular sieve adsorption. The methods are summarized in Table 4-5 and described in greater detail in the following paragraphs. Table 4-6 summarizes typical tail gas analyses from uncontrolled plants and from plants incorporating the two most important NO_x abatement methods in use in new nitric acid plants (catalytic abatement and extended absorption).

4.4.1 Catalytic Reduction

Catalytic reduction has been widely used as an NO_x abatement system installed on new nitric acid plants built since 1971. Catalytic reduction was also used as a method of NO_x decolorization on over 50 percent of nitric acid plants built prior to the NSPS. The reasons for the prevalance of this control technology until 1975* were:

(1) Its relative ease and flexibility of operation

(2) The recovery of waste heat

(3) High NO_x removal efficiencies.

In practice, the catalytic reduction unit is an integral part of the plant (Figure 4-6). The tail gas from the absorption tower is preheated by heat exchange with the converter effluent gas. Fuel is added and burned in the catalytic unit to generate heat and abate

*The advent of a proven alternate NO_x control technology--the extended absorption process--together with the developing natural gas shortage at that time radically changed the entire nitric acid plant NO_x control situation (see Section 4.4.2).

TABLE 4-5

NO_x ABATEMENT METHODS FOR NITRIC ACID PLANTS

Method	Description	Comments
Catalytic Reduction		
Nonselective	Reduction of NO_x and O_2 with CH_4, CO or H_2 over a Pt or Pd catalyst to form N_2, CO_2 and H_2O; single-stage unit reduces NO_2 to NO (decolorization); two-stage unit or single-stage with temperature control reduces NO to N_2 (full abatement).	Prior to the promulgation of NSPS, decolorization of the absorber tail gas was often profitable because of the energy recovered from the combustion of methane; full abatement now requires additional methane and represents a fuel penalty; may be operated at high or low pressure; may be used in conjunction with extended absorption.
Selective	Reduction of NO_x only with NH_3 over a Pt catalyst to form N_2.	Energy recovery not possible; may be operated at high or low pressures; often used with extended absorption.
Extended Absorption	Use of a second absorption column to increase recovery and yield of HNO_3.	Required inlet pressure of 730 kPa may necessitate additional compressor unit.
Wet Scrubbing	Scrubbing absorber tail gases with solution of urea, ammonia, sodium hydroxide, sodium carbonate, or potassium permanganate.	May be operated at low or high pressure, but NO_x removal greater at higher pressures.
Molecular Sieve Adsorption	Removal of NO_x using adsorbent/catalyst bed containing a synthetic zeolite; thermal regeneration recovers NO_2 for conversion to HNO_3.	High energy and capital requirements; achieves extremely low NO_x emissions (<50 ppm).
Chilled Absorption	Chilling absorbing solution to increase NO_2 solubility and yields of HNO_3.	Primarily used as retrofit on existing plants; usually cannot meet NSPS without other controls or lowered acid product concentration.

TABLE 4-6

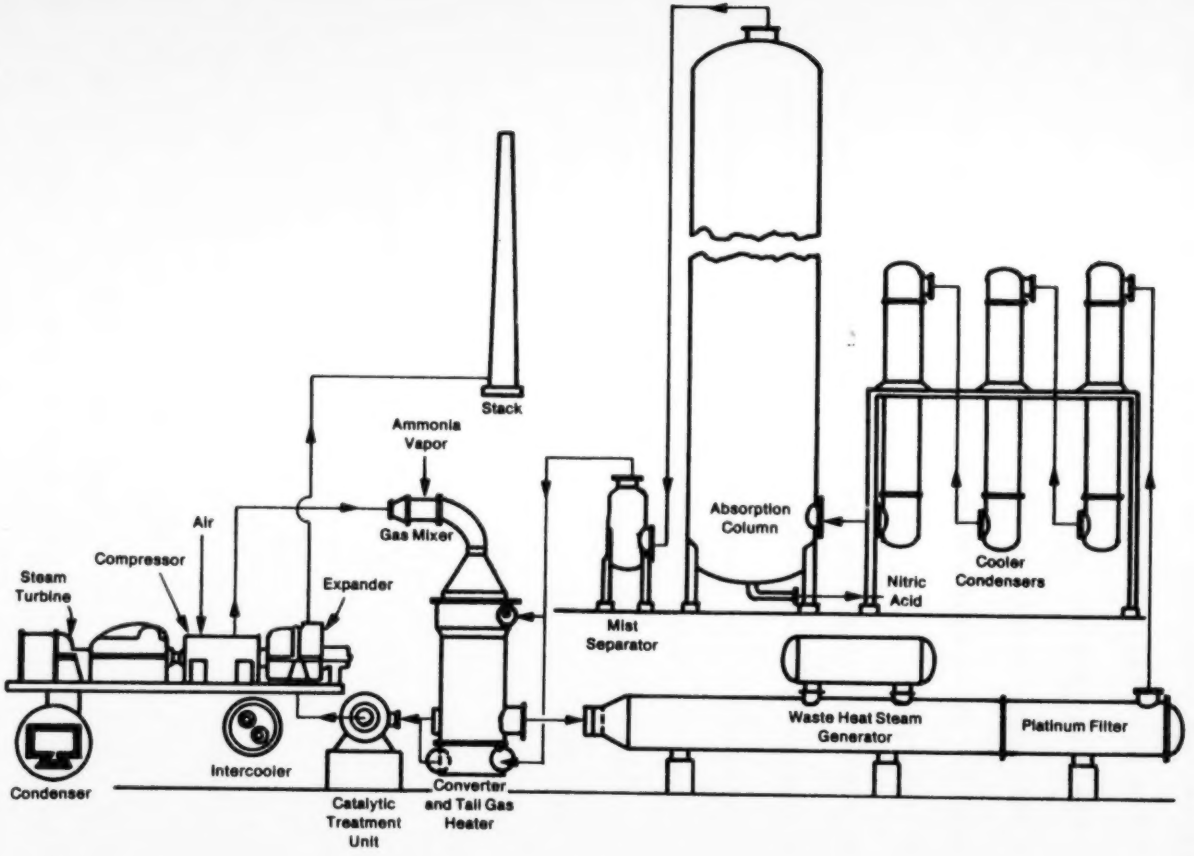
TYPICAL NITRIC ACID PLANT TAIL GAS EMISSION COMPOSITIONS
(Percent by Volume)

Component or Tail Gas	Plant Control Method		
	Uncontrolled[a]	Catalytic Reduction	Extended Absorption[b]
NO	0.10	0.01	-
NO_2	0.15	trace	0.015
N_2	96.15	94.20	96.00
O_2	3.00	trace	3.50
H_2O	0.60	3.80	0.50
CO_2	-	2.00	-

[a]Conventional design has been 98 percent absorption efficiency (this composition is typical of the tail gas before catalytic reduction).

[b]The control in this plant is done by increasing the absorption efficiency to 99.8 percent plus.

Source: Wyatt, 1973.



Source: Wyatt, 1973.

FIGURE 4-6
ACID PLANT INCORPORATING CATALYTIC REDUCTION FOR NO_x ABATEMENT

the tail gas. The hot gas from this unit passes to an expander which drives the process air compressor for the ammonia converter. A waste heat boiler removes the heat from the expander outlet gas in the form of steam, and the treated tail gas is vented to the atmosphere. In some cases, a waste heat boiler is required after the catalytic unit to keep the expander inlet temperature below its design maximum - usually 677°C (1250°F).

Catalytic reduction processes can be divided into two categories: nonselective and selective reduction. In nonselective reduction, the tail gases from the absorber are heated to the necessary ignition temperature and mixed with a fuel such as methane, carbon monoxide, or hydrogen. This mixture is passed to the catalytic reduction unit, where the fuel reacts with both NO_x and O_2 to form CO_2, H_2O and N_2 over a catalyst consisting of 0.5 percent Pt or Pd either in the form of spherical pellets or deposited in a honeycomb ceramic material. When methane (natural gas) is used as the fuel, the following reactions take place:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad (6)$$

$$CH_4 + 4NO_2 \rightarrow 4NO + CO_2 + 2H_2O \quad (7)$$

$$CH_4 + 4NO \rightarrow 2N_2 + CO_2 + 2H_2O \quad (8)$$

The first two of these reactions proceed rapidly with the evolution of considerable heat which is recovered in a waste heat boiler. In the second reaction or decolorization step, the nitrogen dioxide is converted to nitric oxide, so the gas is colorless even though there

has been no decrease in the total nitrogen oxides. Only the reaction with additional methane as shown in the last reaction results in the reduction of the nitric oxide to nitrogen. The final reduction step must be limited to an upper temperature of 843°C (1550°F), due to the catalyst thermal limitation. If reduction has to be carried out in the presence of high oxygen concentrations (above 3.0 percent), it must be performed in two stages to prevent exceeding the upper temperature limit. When this last reaction is complete, total NO_x abatement is achieved.

For a given fuel, there is a minimum ignition temperature required to initiate the reaction. Once reaction has started the heat of reaction will maintain the temperature. Ignition temperature is lowest for hydrogen and carbon monoxide, 150° to 200°C, and highest for natural gas, 480° to 510°C.

In practice, 90 to 95 percent of the nitrogen oxides in the tail gas are decomposed by this process. Typical operating conditions are summarized in Table 4-7. The particular process conditions chosen depend upon the usefulness of recovering heat, the amount of capital available for the cost of heat exchangers and related equipment, and the availability and cost of fuels. Depending on the overall plant heat balance, significant economic return can be realized through recovery of heat generated in the abatement unit.

In the selective reduction process, ammonia is used to catalytically reduce NO_2 to N_2 without simultaneously reacting with

TABLE 4-7

OPERATING CONDITIONS FOR TREATING NITRIC ACID PLANT TAIL GAS BY CATALYTIC REDUCTION

Process Conditions	Nonselective Catalytic Reduction			Selective Catalytic Reduction
Usable fuels	Natural gas, hydrogen coke, oven gas, propane			Ammonia
Assumed fuel	Natural gas			Ammonia
O_2 in tail gas, %	2-3	3-5		2-5
Number of stages	1	2		
		1st stage	2nd stage	
Preferred catalyst	Pd	Pd	Pd	Pt
Space Vel., SCFH/CF	60,000	20,000 to 40,000	60,000	30,000
Mininum Inlet Temperature, °C	460	440 to 500	460	180
Fuel, Volume % of Tail Gas	1.1-1.7	0.8-1.3	0.9-1.4	0.3
Approximate Temperature Rise, °C	130 to remove all O_2 from tail gas containing 1% O_2			20-40

Source: Gillespie et al., 1972.

oxygen. A ceramic-supported (either pellets or honeycomb) platinum catalyst is used to effect the following reactions:

$$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12\ H_2O \quad (9)$$

$$4NH_3 + 6NO \rightarrow 5N_2 + 6\ H_2O \quad (10)$$

Both of these reactions occur at relatively low temperatures (210° to 270°C). Typical operating conditions for selective reduction are summarized in Table 4-7.

The advantage of this method is that less heat is evolved and the installation of heat removal equipment is unnecessary. However, the platinum catalyst required is more expensive and the ammonia cost may not be competitive with other fuels even when less is required. Close temperature control is required to prevent ammonia oxidation, which would increase nitrogen oxide emissions. Start-up and shut-down procedures must also be closely controlled to avoid formation of ammonium nitrite salts.

Catalytic reduction is particularly suited to the pressure ammonia oxidation process in which the absorption tower tail gas is of uniform composition and flow, is under pressure, and can be reheated by heat exchange to the necessary reduction unit feed temperature. Of the 19 nitric acid plants subject to NSPS which are currently on stream, eight feature catalytic reduction as the NO_x control mechanism.

4.4.2 Extended Absorption

The most obvious method of reducing NO_x emissions in the tail gas of a nitric acid plant is to increase the absorption efficiency. Emission control by absorption is somewhat misleading, since no add-on emission control equipment is necessary if the plant is designed and built with sufficient absorption capacity. The majority of nitric acid plants built since World War II have absorbers designed for an absorption efficiency of 98 percent, allowing an emission of 15 to 17.5 kg of NO_x (as NO_2) per metric ton of nitric acid. This design factor was established by economics and the lack of air pollution regulations. However, with present day economics and the advent of the NSPS, designing absorption plants for higher NO_x recovery has received more consideration. Nitric acid plants have been constructed with absorption systems designed for 99.8 plus percent NO_x recovery. This recovery efficiency assures compliance with the NO_x NSPS of 1.5 kg/Mg (3.0 lb/ton).

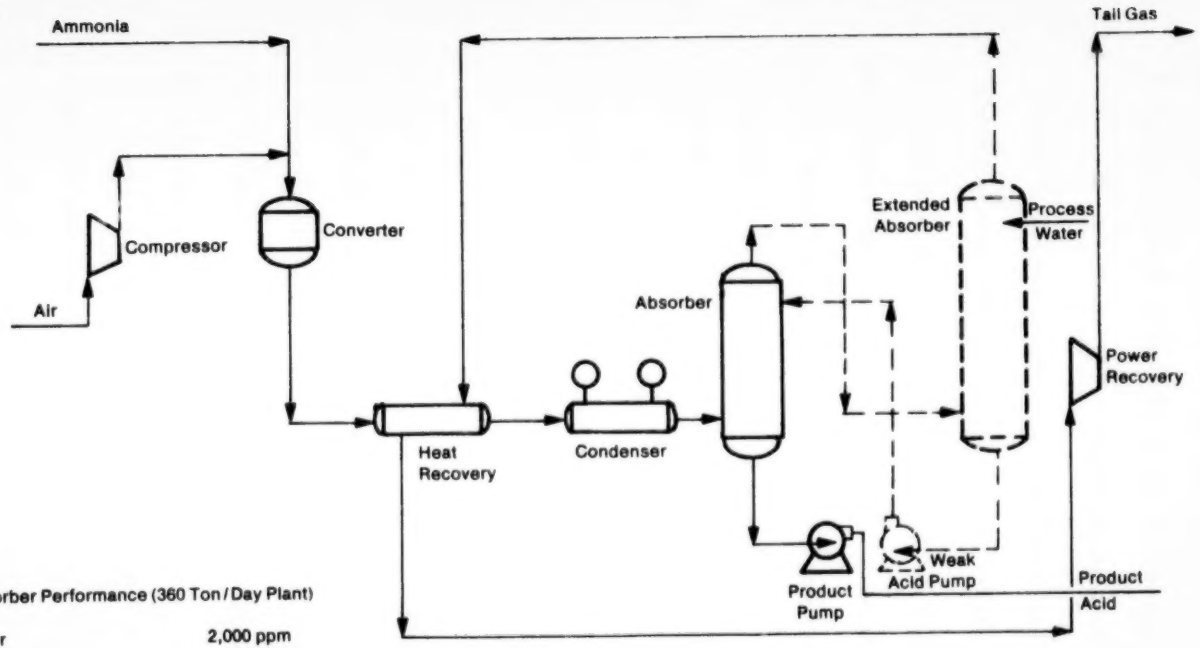
In the extended absorption process, a second absorption tower is added in series to the existing absorber. The NO_x is absorbed by water and forms nitric acid. The economics of the extended absorption process generally require the inlet gas pressure at the absorber to be at least 730 kPa (107 psig). Also, cooling is usually required if the inlet NO_x concentration is above 3000 ppm. There is normally no liquid effluent from extended absorption; the weak acid from

the secondary absorber is recycled to the first absorber, increasing the yield of nitric acid. Figure 4-7 is a schematic flow sheet of a 328 Mg/day (360 tons/day) nitric acid plant using extended absorption. Also shown on Figure 4-7 are the operating conditions and utility requirements in effect at this plant. The system shown is the Grande Paroisse* version of the extended absorption process.

In the D.M. Weatherly Company version of the extended absorption system, a smaller volume and number of trays in the absorption system is required as compared with the Grande Paroisse absorption system due to the use of mechanical refrigeration for chilling part of the cooling water employed. Two cooling water systems are used for cooling the absorbers. The first part of the absorption process is cooled by the normal cooling water available at the plant site. Approximately one-third of the trays are cooled by normal cooling water. The balance of the trays in the absorption system, are cooled by cooling water at about 7°C (45°F), which is achieved by mechanical refrigeration. The refrigeration process is a part of the ammonia vaporization section of the nitric acid plant (Weatherly, 1976).

The extended absorption system operates without any problems as long as design conditions are met. This means that the absorber pressure and oxygen content in the gas to the absorber must not be below design level; and the temperature and NO_x content in the gas stream must not exceed design level. With regard to temperatures,

*Licensed by the J.F. Pritchard Co., Kansas City, MO.



Extended Absorber Performance (360 Ton/Day Plant)

NO_x Inlet Tower	2,000 ppm
NO_x Exit Tower	180 ppm
Tower Pressure Drop	4.5 psi
Cooling Water	150 gpm
Electric Power	180 kW*
Catalyst	0
Fuel (Additional)	0
Maintenance (Additional)	0
Process Water (Additional)	0
Operations Man Hours (Additional)	0
Additional Production	6.1 Tons/Day

* 88 kW Required to Offset 4.5 psi Pressure Drop.

Source: EPA, 1976.

FIGURE 4-7
EXTENDED ABSORPTION SYSTEM
FOR NO_x EMISSIONS CONTROL

this system is particularly vulnerable to high summer ambient temperatures in the southern tier of states, i.e., temperatures in excess of 95° to 100°F. Information from one extended absorption nitric acid plant in Louisiana for the third quarter of 1978 seems to confirm this problem. In August there were 2 days when 4-hour periods of excess NO_x emissions occurred due to high ambient temperatures (Carville, 1978). Since the NO_x vapor pressures can be higher then the absorber can cope with during these periods of excessive ambient temperatures, one extended absorption system vendor will guarantee performance within the specified NO_x emission limit only 95 percent of the time (Russell, 1978).

Of the 19 nitric acid plants currently subject to NSPS, nine feature extended absorption as the NO_x control mechanism. It is noteworthy that eight of these nine plants have come on stream since the energy crisis of the mid-1970s.* Additionally, seven of the eight plants scheduled to come on stream by the end of 1979 (Table 4-2) feature extended absorption for NO_x emission control. It appears that from a day-to-day operational standpoint, nitric acid plant operators have decided that the increasing uncertainty of an adequate natural gas supply, the principal fuel used in the catalytic reduction units, together with the anticipated sharp increases in natural gas price over the next few years,** have made extended

*One of these plants (a U.S. Army installation) operates intermittently and is currently down.

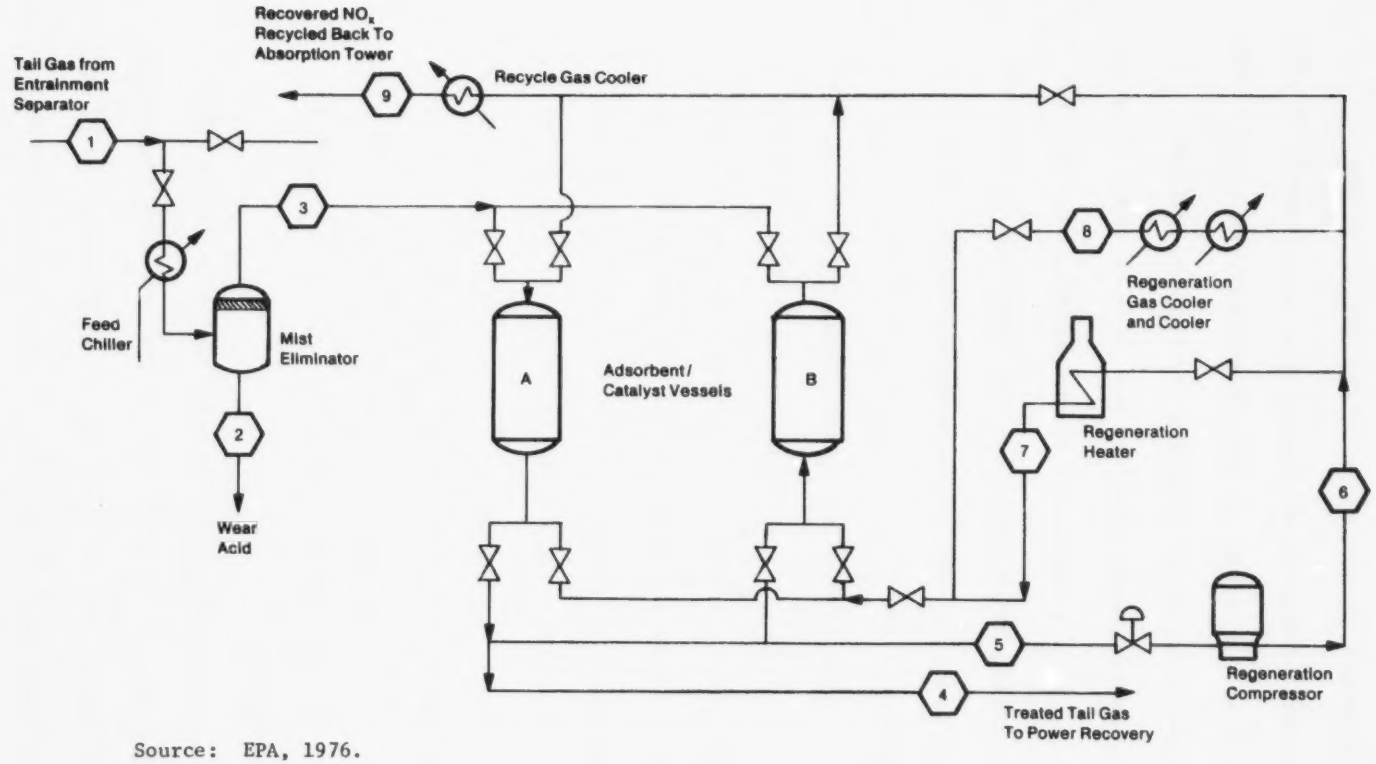
**Interstate natural gas price (old gas) is expected to be in the $1.50 to $2.00 per 1000 cubic feet range in the early 1980s, as compared with the present price of approximately $1.25 per 1000 cubic feet (MITRE estimate).

absorption the preferred process for NO_x abatement in the future. In cases where the new nitric acid plant is located in a fertilizer complex* with an available contract at favorable prices an assured low-price, long-term natural gas supply, catalytic reduction economics are more attractive than extended absorption, provided that fuel consumption is only slightly in excess of the stoichiometric amount needed for NO_x abatement (Byrne, 1978).

4.4.3 Molecular Sieves**

Molecular sieves can selectively adsorb NO_x from nitric acid plant tail gas. NO_x removal is accomplished in a fixed bed adsorption/catalyst system, providing recovery and recycle of the nitrogen oxides back to the nitric acid plant absorption tower. A flow diagram for a Purasiv*** control system is shown in Figure 4-8. The water-saturated nitric acid plant absorption tower overhead stream is chilled to 7° to 10°C (45° to 50°F), the exact temperature level being a function of the NO_x concentration in the tail gas stream, and passed through a mist eliminator to remove entrained water and acid mist. The condensed water, which absorbs some of the NO_2 in the tail gas to form a weak acid, is collected in the mist eliminator and either recycled to the absorption tower or sent to storage. The dried tail gas then passes through a molecular sieve bed where the special properties of the NO_x removal grade molecular sieve result

*Where ammonia is synthesized from natural gas.
**This information is taken from EPA, 1976, unless otherwise noted.
***Purasiv is the molecular sieve system developed by Union Carbide Corp.



Source: EPA, 1976.

FIGURE 4-8
TWO-BED PURASIV N PROCESS (VESSEL A UNDER ADSORPTION AND VESSEL B UNDER REGENERATION HEATING) FOR CONTROL OF NO_x IN NITRIC ACID PLANT TAIL GAS

in the catalytic conversion of NO to NO_2. This occurs in the presence of the low concentrations of oxygen typically present in the tail gas stream. Nitrogen dioxide is then selectively adsorbed. The molecular sieve adsorbent/catalyst provides the most effective performance and longest life when the tail gas is bone dry. This is accomplished by drying with a desiccant which exhibits very little coadsorption of NO_x during water removal. The desiccant is located in the same adsorber vessel as the NO_x adsorbent/catalyst in a compound bed arrangement.

Regeneration is accomplished by thermal swinging (cycling) the adsorbent/catalyst bed after it completes its adsorption step and contains a high adsorption loading of NO_2. The required regeneration gas is obtained by heating a portion of the treated tail gas stream which is then used to desorb the adsorbed NO_2 from the bed for recycle back to the nitric acid plant absorption tower. The treated tail gas stream is passed through an oil or gas-fired heater to provide heat for regeneration. The NO_2-loaded gas is recycled to the nitric acid absorption tower. The pressure drop in the sieve bed averages 34 kPa and NO_x outlet concentration of the molecular stack gas averages 50 ppm.

The process has been successful in meeting NO_x emission standards for existing plants. The principal criticisms have been high capital and energy costs, and the problems of coupling a cyclic system to a continuous acid plant operation. Furthermore, molecular

sieves are not considered as state-of-the-art technology (Acurex/ Aerotherm, 1977).

There have been no nitric acid plants built and subject to NSPS which incorporate molecular sieves as NO_x control technology.

4.4.4 Wet Scrubbing

Wet scrubbing involves treatment of the absorber tail gas with solutions of alkali hydroxides or carbonates, ammonia, urea, or potassium permanganate to absorb NO and NO_2 in the form of nitrate and/or nitrite salts in a scrubbing tower. In the case of caustic scrubbing, the following reactions take place:

$$2NaOH + 3NO_2 \rightarrow 2NaNO_3 + NO + H_2O \quad (11)$$

$$2NaOH + NO + NO_2 \rightarrow 2NaNO_2 + H_2O \quad (12)$$

However, disposal of the spent scrubbing solution presents a serious water pollution problem. One nitric acid plant subject to NSPS employs a combination of chilled absorption and caustic scrubbing to achieve NO_x abatement.

One of the more novel scrubbing processes uses a urea solution to convert the nitrogen oxides, after oxidation to their respective acids, to nitrogen and marketable ammonium nitrate:

$$HNO_2 + CO(NH_2)_2 + HNO_3 \rightarrow N_2 + CO_2 + NH_4NO_3 + H_2O \quad (13)$$

This process has been reported to reduce NO_x emissions from 4000 ppm to 100 ppm and can theoretically be designed for no liquid effluent; in practice, however, some effluent is produced requiring wastewater treatment. Additionally, marketing of the ammonium nitrate is not always possible, creating an additional storage/disposal problem.

5.0 INDICATIONS FROM NSPS COMPLIANCE TEST RESULTS

5.1 Test Results from EPA Regional Sources

The MITRE Corporation, Metrek Division, conducted a survey of all 10 EPA regions to gather available NSPS compliance test data for each of the 10 industries under review (MITRE Corp., 1978). This survey yielded test data on two new nitric acid units. Data included average NO_x emissions and 100 percent nitric acid production rates for these units in effect at the time of the test. In both cases, the nitric acid production rate was at the unit design maximum (the actual production rates were within 5 to 10 percent of the nominal design rates). The two units were stated to be in compliance with respect to the opacity standard. Telephone contacts with EPA regional personnel, nitric acid plant operators and a search of the literature yielded NSPS compliance test data on an additional 12 new nitric acid units. Five new operational nitric acid units have not been tested for compliance under NSPS as of August, 1978. In all, 14 sets of data were obtained representing 14 new or modified nitric acid units.

5.2 Analysis of NSPS Test Results

The NO_x emission results of the NSPS compliance tests obtained for the 14 nitric acid units are tabulated in Table 5-1 and displayed in Figure 5-1. It should be noted that the data in Figure 5-1 are displayed in terms of the three NO_x control technologies used at all of the plants subject to NSPS.

TABLE 5-1

NSPS COMPLIANCE TEST RESULTS FOR HNO_3 PLANTS

EPA Region	Company	Plant Location	Nominal Unit Size (100% HNO_3) Mg/day (TPD)	Average NO_x Emissions Kg/Mg of 100% HNO_3 (lb/ton)	Actual Plant Production Rate During NSPS Test Mg/day 100% HNO_3 (TPD)	Measured Opacity During Test (%)	Emission Control System	Reference
III	Allied Chemical Corp.	Newell, Penn.	164 (180)	0.27 (0.54)	155 (170)		Catalytic Reduction	Bland, 1978
IV	Monsanto Textile Co.	Escambia City, Fla.	815 (900)	a	a	a	a	—
	Nitram, Inc.	Tampa, Fla.	320 (356)	0.61 (1.22)	320 (350)	0	Catalytic Reduction	Thompson, 1978
	Columbian Nitrogen	Augusta, Ga.	815 (900)	0.25 (0.5)	980 (1077)	0	Catalytic Reduction	Gardner, 1978
	Kaiser Aluminum Chemical	Savannah, Ga.	450 (500)	1.24 (2.49)	495 (544)	<10	Extended Absorption	EPA CDS, 1978[c]
	Mississippi Chemical	Yazoo City, Miss.	910 (1000)	1.25 (2.50)	850 (937)	<10	Extended Absorption	Stark, 1978
			328 (360)	1.35 (2.70)	328 (360)		Extended Absorption	Brown, 1976
	U.S. Army	Holston, Tenn.	273 (300)	~1.50 (~3.0)[b]	287 (315)		Extended Absorption	Dezariac, 1978
VI	CF Industries	Donaldsonville, La.	470 (520)	0.44 (0.88)	460 (506)	<10	Extended Absorption	Carville, 1978
	Allied Chemical Corp.	Geismar, La.	500 (550)	a	a	a	Extended Absorption	—
	Rubicon Chemical	Geismar, La.	320 (350)	0.069 (0.138)	240 (265)		Catalytic Reduction	EPA CDS, 1978
	IMC - Dixie Chemical	Sterlington, La.	200 (220)	0.41 (0.83)	190 (209)		Extended Absorption	EPA CDS, 1978
	Agrico Chemical Co.	Catoosa, Okla.	570 (630)	1.07 (2.15)	630 (692)		Chilled Absorption & Caustic Scrubbing	Murphy, 1978
	Air Products & Chemical	Pasadena, Tex.	289 (318)	0.24 (0.48)	278 (306)		Catalytic Reduction	Spruiell, 1978
	Dupont Co.	Victoria, Tex.	910 (1000)	0.78 (1.55)	955 (1049)	<5	Extended Absorption	Russell, 1978
IX	Union Oil Co. of Calif.	Brea, Calif.	135 (150)	0.024 (0.047)	150 (163)		Catalytic Reduction	Waddell, 1978
	Valley Nitrogen	Fresno, Calif.	180 (200)	a	a	a	Catalytic Reduction	—
X	J.R. Simplot Co.	Pocatello, Idaho	48 (53)	0.031 (0.063)	50 (55)		Catalytic Reduction	Wolleson, 1978
	Chevron Chemical Corp.	Kennewick, Wash.	500 (550)	1.0 (2.0)[b]	500 (550)		Extended Absorption	Spaniel, 1978

[a] Not yet tested under NSPS.

[b] Not an official NSPS test.

[c] Compliance Data System.

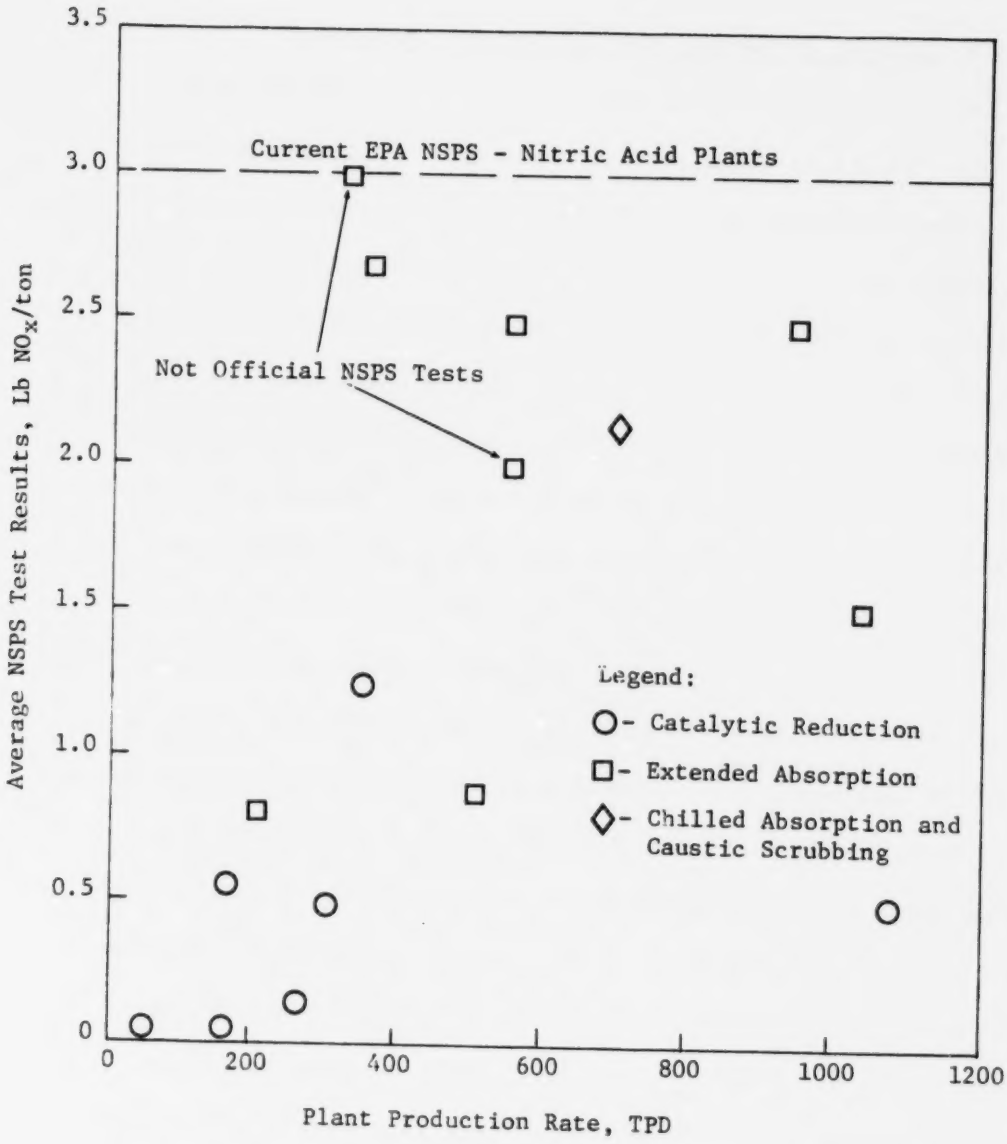


FIGURE 5-1
NITRIC ACID PLANTS NSPS TEST RESULTS
NO_x EMISSIONS

5.2.1 Control Technology Used to Achieve Compliance

All 14 units tested showed compliance with the NSPS NO_x control level. Of the 14 units tested, seven achieved compliance with the NO_x standard through use of the catalytic reduction process.* Of the remaining seven units, six use the extended absorption process and one employs a combination of chilled absorption and caustic scrubbing to meet the standard. All of the new units meet the opacity standard since opacity is directly related to NO_x emissions.

It is evident from Figure 5-1 that catalytic reduction is more capable of control to lower NO_x emission levels than extended absorption. The arithmetic average of the NSPS NO_x control results is 0.22 kg/Mg of 100 percent acid (0.44 lb/ton) where catalytic reduction control technology is employed, while the arithmetic average of the NSPS test results for those plants using extended absorption, is 0.91 kg/Mg of 100 percent acid (1.82 lb/ton). Thus, both technologies can meet the present NSPS for NO_x emissions. However, as was discussed in Section 4.4.2, it is likely that the great majority of nitric acid plants built in the future will employ extended absorption as the NO_x control technology. Since extended absorption absorption was not in use in any U.S. nitric acid plants at the time

*Most of these plants use the nonselective catalytic reduction process. At least one plant uses the selective process (distinctions between these processes are discussed in Section 4.4.1). All references to catalytic reduction in later sections of this report refer to the nonselective process.

of promulgation of the NO_x NSPS, EPA had only described catalytic reduction as the control technology capable of achieving compliance with the standard. With the demonstrated ability of extended absorption to control NO_x emissions to within the present standard, and the very pronounced trend to this technology for NO_x control in future plants, any changes in the NSPS must be considered in the light of this newer technology.

5.2.2 Comparative Economics of the Catalytic Reduction and Extended Absorption Processes for NO_x Abatement

Relative costs of new nitric acid plants equipped with either catalytic reduction or extended absorption processes for NO_x control, have been developed and are shown in Table 5-2. The costs shown are in 1975 dollars.

Study of Table 5-2 indicates that in terms of 1975 dollars, the total annual operating cost of the catalytic reduction process is approximately 98 percent of this cost for extended absorption. Escalation to current costs would affect both catalytic abatement and extended absorption in similar amounts for nearly all the items shown in the determination of total annual operating cost. However, the fuel cost shown for catalytic reduction, i.e., $1.00/million BTUs for natural gas, is not a realistic current cost. A MITRE estimate for a realistic volume price for interstate natural gas at present would be in the neighborhood of $1.25/million BTUs. This price is likely to increase sharply in the near future. On this basis, the

TABLE 5-2

COST OF PRODUCING NITRIC ACID USING CATALYTIC REDUCTION AND EXTENDED ABSORPTION NO_x CONTROL METHODS FOR A 500-TON/DAY PLANT

Item	Unit		Quantity/ton Product		Cost/Unit		Cost/ton Product	
	CRP[a]	EAP[b]	CRP	EAP	CRP	EAP	CRP	EAP
Raw Material & Catalyst								
Ammonia	Tons	Tons	0.292	0.2876	140.00	140.00	40.88	40.14
NO_x Reduction Catalyst	Dollars						0.30	
Utility Consumption								
Cooling Water	M.Gal	M.Gal	22.0	30.0	0.02	0.02	0.44	0.60
Steam (Credit)	M.Lb		2.2		1.33		(2.93)	
Steam		M.Lb		0.30		1.33	0.15	0.40
Electricity	KWH		15	40	0.01	0.01		0.40
Fuel	$1x10^6$BTU		2.30		1.00		2.30	
Other Cost								
Maintenance	Dollars	Dollars					0.91	1.09
Depreciation	Dollars	Dollars					2.42	2.91
Operating Labor	Dollars	Dollars					0.40	0.50
			TOTAL ANNUAL OPERATING COST				44.87	46.04

Basis	CRP	EAP
Investment Cost	$ 6,000,000	$ 7,200,000
Production	165,000 Tons/Yr	165,000 Tons/Yr
Maintenance	$150,000/Yr	$180,000/Yr
Depreciation	15 Yr	15 Yr
Operating Labor	4400 Man-Hrs/Yr	5500 Man-Hrs/Yr
Labor Rate	$15/Hr	$15/Hr

[a] Catalytic Reduction Process
[b] Extended Absorption Process

Source: Weatherly, 1976.

total annual operating cost (in current dollars) for the catalytic abatement and extended absorption processes appears to be quite comparable. However, the investment cost for extended absorption appears to be appreciably greater than that for catalytic abatement based on data in Table 5-2.

5.3 Indications of the Need for a Revised Standard

At this time, there is not sufficient justification for making the present NO_x NSPS (and the related opacity standard) more stringent, based on the following considerations:

- There are several alternative NO_x control technologies available to the nitric acid industry, two of which have been the control systems of choice since the promulation of the nitric acid plant NSPS. These are catalytic reduction and extended absorption

- Of these two systems, NSPS compliance test data have clearly shown that catalytic reduction is the best demonstrated control technology (even though both NO_x control systems meet the present NSPS), since this system of NO_x control produces a much lower level of residual NO_x in the exhaust gas than extended absorption (based on NSPS compliance test data). Additionally, catalytic reduction is a much more flexible system than extended absorption in that it can deal with upset conditions in the nitric acid plant which produce large NO_x excursions in a much more efficient manner.*

- However, the overriding consideration in determining choice of NO_x control systems at the present time and in both near and long term, is the uncertainty of supply and sharply escalating cost of natural gas -- the principal fuel used in the catalytic reduction process. For this reason, nitric acid producers have opted for extended absorption NO_x control in about 50 percent of the plants built in the last 4 years (through mid-1978) and will have incorporated extended absorption NO_x control in about 90 percent of new plants to be completed by

*Section 6.2 presents data on NO_x emissions resulting from upset conditions.

1980. On the basis of annualized costs, the catalytic reduction and extended absorption NO_x control process appear to be comparable, so that there would be minimal cost penalty for new nitric acid plants incorporating the extended absorption process.

- While the extended absorption process can maintain NO_x emissions at levels below the present standard, the emission levels achieved do not represent a very large margin of safety. A principal vendor of this equipment provides a normal performace guarantee of 200 ppm of NO_x in the nitric acid absorber tail gas (equivalent to approximately 3 lb/ton) with only a 7 to 8 percent margin of safety in terms of absorber tray count. The lowest performance guarantee which has been provided by this vendor, is 150 ppm NO_x (equivalent to approximately 2.25 lb/ton) in the latest plant design. Absorption towers get very large and costly as the performance guarantee on NO_x emission level is tightened (Russell, 1978). Thus, limitations in extended absorption performance appear to preclude making the NSPS more stringent at the present time.

Other considerations, including effect of projected nitric acid plant construction on NO_x emissions and unique features of extended absorption which affect the NSPS, are discussed in Section 6.0.

6.0 ANALYSIS OF THE IMPACTS OF OTHER ISSUES ON THE NSPS

6.1 Effect of Projected Nitric Acid Plant Construction on Emissions

Based on the information presented in Section 4.1, the rate of completion of new or modified nitric acid plants during the 1971 to mid-1978 period has been approximately two to three per year. During mid-1978 to 1980 period, the number of new nitric acid plants planned or under construction continues to average about the same as the previous period. Based on this information, and an anticipated slowdown in nitrogen-based fertilizer exports during the early 1980s (Chemical and Engineering News, 1978), MITRE estimates a maximum of two new nitric facilities added to existing U.S. production capacity during the 1980-1983 period. This will result in a maximum of eight new nitric acid production lines starting up during this 4-year period. In addition, replacement of older nitric acid plants during this period is assumed to occur at the same rate, i.e., eight replacement units are anticipated to start-up during the 1980 to 1983 period. Thus, a total of 16 nitric acid units subject to NSPS, are predicted to come on-line during this period. Based on data in Tables 4-2 and 4-6 these new units are expected to average about 423 Mg/day (465 tons/day) each.

The total NO_x emissions have been calculated at various NSPS emission control levels for the 16 new units projected to be completed during the 1980-1983 period. The results of these calculations are shown in Table 6-1.

Table 6-1 indicates that halving the present NSPS control level from 1.5 Kg/Mg (3.0 lb/ton) to 0.75 Kg/Mg (1.5 lb/ton) would have a relatively small effect on total U.S. NO_x emissions, considering both the relation to total emissions from NSPS-controlled plants and to total emissions from all stationary sources. Approximately 1800 Mg/Yr (2000 tons/year) reduction in total NO_x emissions from NSPS-controlled plants, results from a 50-percent reduction in the NSPS control level. The relative national environmental impact of these projected new nitric acid plants comparing the present NO_x NSPS control level and a 50 percent reduction of this level is very small when considered against the total NO_x emissions from all stationary sources.

6.2 Problems Encountered by the Extended Absorption Process in Controlling NO_x Emissions

The extended absorption process appears to be capable of controlling NO_x emissions from nitric acid plants subject to NSPS, to less than 1.5 kg/Mg (3.0 lb/ton) during normal operation, based on NSPS compliance test results (see Section 5.0). However, communication with extended absorption nitric acid plant operators indicates that problems are encountered during startup (where process malfunctions may exist for several hours requiring several restarts) and shutdown (particularly unscheduled or emergency shutdown). During these periods process conditions are unstable, and NO_x emission concentrations tend to be high while production is low

TABLE 6-1

PROJECTED CUMULATIVE NO_x EMISSIONS FROM NEW & REPLACEMENT NITRIC ACID PLANTS ADDED BETWEEN 1980 AND 1983[a]

Control Level Kg/Mg (lb/ton)	Projected Emissions Mg/Yr (ton/Yr)[b] 1980	1981	1982	1983	Percent of Total Annual NO_x Emissions of NSPS Nitric Acid Plants in 1983[c]	Percent of Total Annual NO_x Emissions of All Stationary Sources in 1983[d]
1.5 (3.0)	890 (980)	1780 (1960)	2680 (2940)	3570 (3920)	38.1	0.024
1.25 (2.5)	740 (810)	1470 (1620)	2190 (2410)	2950 (3240)	33.8	0.020
1.0 (2.0)	590 (650)	1180 (1300)	1770 (1950)	2370 (2600)	29.1	0.016
0.75 (1.5)	450 (490)	890 (980)	1340 (1470)	1780 (1960)	23.6	0.012
0.50 (1.0)	300 (325)	590 (650)	890 (975)	1270 (1400)	18.1	0.009

[a] Four nitric acid plants (average production capacity of 423 Mg/day (465 tons/day) of 100% HNO_3 each) are projected to be installed per year from 1980 to 1983, inclusive.

[b] Calculations based on a 350-day work year.

[c] Total annual NO_x emissions of 26 existing NSPS HNO_3 units in 1983 (at present 3.0 lb/ton control level) are 5780 Mg/Yr (6350 tons/yr).

[d] Total NO_x emissions from all stationary sources are projected as 14.6 MM Mg/Yr (16 MM tons/yr) in 1983, based on existing NSPS and state standards in effect prior to 1975 (EPA, 1976a).

or nonexistent. No external control system is available in these situations to reduce NO_x emissions to below the control level (as in the catalytic reduction process), and a period of excess emissions occurs. Limited data from two plants in their third quarter, 1978 excess emissions reports to EPA Region VI illustrate this problem (Tables 6-2 and 6-3).

TABLE 6-2

EXCESS EMISSIONS DATA FROM EXTENDED ABSORPTION
NITRIC ACID PLANT OPERATIONS

Plant: CF Industries, Donaldsonville, LA[a,b]

Date	Time Period	Emissions Lb. NO_x Per Ton of 100% HNO_3	Cause
7/2/78	12-1 pm 1-2 pm 2-3 pm 3-4 pm	3.83 4.52 4.26 3.52	Start up
7/11/78	6-7 pm 7-8 pm 8-9 pm	5.89 4.99 4.15	Start up followed shutdown due to expander bypass valve malfunction
7/23/78	2-3 pm 3-4 pm 4-5 pm	5.71 6.65 3.76	Start up
8/7/78	3-4 pm 4-5 pm 5-6 pm 6-7 pm 7-8 pm	4.27 4.23 3.27 5.20 3.48	Start up followed shutdown due to high guage temperature trip
8/16/78	6-7 pm 7-8 pm 8-9 pm	4.25 5.65 2.32	Start up followed shutdown due to NO_x compressor trip
8/20/78	11-12 am 12-1 pm 1-2 pm 2-3 pm	2.81 3.29 3.40 3.07	Reduced absorption tower efficiency due to high ambient temperature
8/22/78	11-12 am 12-1 pm 1-2 pm 2-3 pm	2.88 3.23 3.24 3.00	Reduced absorption tower efficiency due to high ambient temperatures
8/24/78	1-2 pm 2-3 pm 3-4 pm	5.49 4.17 3.74	Start up followed shutdown due to NO_x compressor trip
8/25/78	1-2 pm 2-3 pm 3-4 pm	4.25 2.89 2.46	Start up followed shutdown due to mysterious trip
8/29/78	5-6 pm 6-7 pm 7-8 pm	3.23 2.63 3.55	Start up followed shutdown due to electrical power failure

a. Increased emissions occur during start ups due to lag time in establishing required absorption tower pressure and lowered circulating water temperature. No external NO_x abatement system is used at this acid plant.

b. Pounds of NO_x are calculated based on 225 ppm(v) equal to 3 lbs/ton at 100 percent production rate.

Source: Carville, 1978.

TABLE 6-3

EXCESS EMISSIONS DATA FROM EXTENDED ABSORPTION
NITRIC ACID PLANT OPERATIONS

Plant: IMC Corp Fertilizer Group, Sterlington, LA

Date	Time Period	Average Emissions Lb. NO_x Per Ton of 100% HNO_3	Cause*
7/7/78	1500-2030	3.7	3 NH_3 Compressor Trips
7/12/78	2330-0230	3.8	Malfunctioning NH_3 drum level control
7/24/78	0200-0500 1100-1815	4.5 3.9	Malfunctioning NH_3 drum level control Malfunctioning NH_3 drum level control
8/5/78	2100-2400	3.1	Start up problems

*Each of these periods was characterized by prolonged start ups caused by instrumentation problems.

Source: Bain, 1978.

7.0 FINDINGS AND RECOMMENDATIONS

The primary objective of the report has been to assess the need for revision of the existing NSPS for nitric acid plants, including a review of the NO_x standard. The existing opacity standard is directly related to the NO_x standard and is not reviewed separately. The findings and recommendations developed in this area are presented below.

7.1 Findings

- The best demonstrated NO_x control technology used in the rationale for the original standard, the nonselective catalytic reduction process, has been largely supplanted in the last few years by a new control process--extended absorption--due to increasing cost and shortages of the principal fuel (natural gas) used in the former process. Based on this overriding consideration it appears that the NOx control process of choice by the nitric acid industry for at least the next few years will be the extended absorption process.

- Both catalytic reduction and extended absorption processes can achieve NO_x emission control levels below the 1.5 kg/Mg (3 lb/ton) standard, based on NSPS compliance test results. The average of seven sets of test data from catalytic reduction controlled plants is 0.22 kg/Mg (0.44 lb/ton), and the average of six sets of test data from extended absorption controlled plants is 0.91 kg/Mg (1.82 lb/ton). Thus, catalytic reduction appears to be capable of controlling NO_x emissions to a level approximately four times lower than the extended absorption process based on NSPS compliance test results. In all cases, the observed opacity was equal to or less than the opacity standard.

- Based on available information on the NO_x emission control capability of the extended absorption process and performance guarantees from a principal vendor of this process, there does not appear to be enough of a safety factor available in the extended absorption process to permit any substantial increase in stringency of the NO_x standard at this time.

- While use of the extended absorption process for NO_x control in new nitric acid plants will not cause any appreciable economic penalty as compared with the use of catalytic reduction in meeting the present NO_x NSPS, making the standard more stringent would involve greatly increased capital costs for the former process since much larger absorption towers would have to be incorporated in the new plants in order to meet tighter performance guarantees. Investment cost for a plant incorporating the extended absorption process may be as much as 20 percent greater than that for a nitric acid plant with a catalytic reduction NO_x control unit installed making the catalytic reduction controlled plant less capital-intensive.

7.2 Recommendations

At this time it is recommended that no change be made in the NO_x NSPS for nitric acid plants. The overriding consideration leading to this recommendation is that sharply escalating cost and developing long-term shortages of natural gas -- the principal fuel used in the catalytic reduction process for NO_x control -- have caused the nitric acid industry to switch to the extended absorption process for NO_x control. Approximately 50 percent of nitric acid plants subject to NSPS built in the last 4 years and 90 percent of plants to be completed by 1980 will have incorporated the extended absorption process for NO_x control.

It is further recommended that an in-depth EPA study be carried out to completely define the NO_x control capability of the extended absorption process before any future consideration can be given to making the current NO_x NSPS more stringent.

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